

10/594017

IAP9 Rec'd PCT/PTO 25 SEP 2006

Recently, a process has been proposed which is based on a chloride acid leach as opposed to a sulfuric acid leach. Whilst a chloride leaching medium is a powerful lixiviant, it is corrosive and requires apparatus to be chloride resistant. Chloride media have also been avoided because they have a high acid consumption and can present difficulties with the control of iron and magnesium leaching, both metals typically present in laterites.

The company Chesbar Resources (now known as Jaguar Nickel Inc.) presented a paper at the ALTA 2002 Conference (Nickel/Cobalt-9 session) in Perth, Western Australia on May 18-20, 2003. The paper entitled "Beyond PAL: The Chesbar Option, AAL" outlined a process for the atmospheric chloride acid leaching of nickel laterite ores. The process is now disclosed in WO 2004/101833.

The Chesbar process requires the use of a pyrohydrolysis stage to regenerate from the process liquor HCl as a gas for recycle to leaching, and to regenerate magnesium oxide for use in a nickel/cobalt precipitation stage. However, HCl gas is difficult to handle, being highly corrosive. In addition, a pyrohydrolysis stage is endothermic, requiring the input of significant energy, and hence has both high capital and operating costs.

It would be advantageous if a halide based process could be provided for the recovery from oxidised metalliferous materials of metals such as nickel, cobalt, copper, precious metals, magnesium etc, which does not require a pyrohydrolysis stage and which does not require recycle of a corrosive gas for the acid leaching stage.

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SUMMARY OF THE DISCLOSURE

In a first aspect there is provided a process for recovering a target metal from an oxidised metalliferous material, the process comprising the steps of:

- 5 - in an acid generation stage, adding sulfuric acid to a solution comprising a metal halide to generate an acidic aqueous halide solution;
- in a leaching stage that is separate to the acid generation stage, leaching the oxidised metalliferous material with the acidic aqueous halide solution to leach the target metal into solution;
- 10 - passing the solution from the leaching stage to a target metal recovery stage in which the target metal is recovered from the solution whilst the metal halide is retained in solution; and
- 15 - returning the solution with the metal halide therein from the target metal recovery stage to the acid generation stage.

The process thus generates an acidic aqueous halide solution, rather than employing sulfuric acid leaching. The resultant halide based leaching process is typically operated at atmospheric pressures. Whilst elevated leaching pressures can be employed (eg. using autoclave leaching) this will depend on the oxidised metalliferous material to be leached and whether more rapid target metal extraction is required.

Further, the addition of sulfuric acid to generate the acidic aqueous halide solution is exothermic and hence allows the pyrohydrolysis stage of the prior art to be eliminated. This part of the process also avoids the recycling of hydrogen chloride gas as per the prior art. Thus, sulfuric acid addition and acidic aqueous halide solution generation can provide substantial savings in capital and operating costs, typically well in excess of the cost of producing sulfuric acid.

However, in applications such as the treatment of electrolytic zinc plant residues, sulfuric acid is a by-product of the electrolytic zinc plant process, so the acid can then be utilised economically in the process for treatment of such residues.

Where a sulfuric acid plant is employed to produce the sulfuric acid for addition to the present process, such plants produce massive amounts of excess heat (ie. as a result of exothermic reactions) which can then be used to heat the process solution, to provide further savings in capital and operating costs.

Depending on the oxidised metalliferous material to be treated, the target metal can include nickel, cobalt, zinc, copper, arsenic, iron, magnesium, precious metals such as gold, silver, platinum etc.

Usually the metal selected for the metal halide solution is one that does not interfere with leaching of the target metal or its recovery as a precipitate. A metal may be selected that forms a precipitate with the sulfate anion of the acid such that, with the generation of the leaching solution, a hydrohalous acid forms together with a precipitate of the metal sulfate. In this regard, the metal may be calcium so that the metal sulfate precipitate is calcium sulfate, which can then form a saleable by-product. However, sodium can be present as a solution metal where the halide is derived from a sodium halide salt. In addition, magnesium chloride may also be used when the material contains high levels of magnesium (eg. to suppress Mg extraction).

Usually and expediently the halide of the metal halide solution is chloride, again because of the abundance of low cost chloride salts such as NaCl. Hence, hydrochloric acid will continuously be formed as the

solution metal precipitates with the sulfate, without the need to form and add or recycle hydrogen chloride gas, as in the prior art. This avoids the handling difficulties and hazards associated with hydrogen chloride gas.

5 However, other halides such as bromide or iodide can be employed, for example, where the metalliferous material includes precious metals. In this regard NaBr may then also be added to the solution, as bromide complexes more strongly than chloride and hence can stabilise the

10 precious metals in solution.

In one form the acid generation stage is defined by a second leaching stage in which both acid generation, and secondary leaching of the oxidised metalliferous material takes place.

15 In one form the sulfuric acid can be added directly to the second leaching stage. Again, the metal of the metal halide solution can be one that forms a precipitate with the sulfate anion of the sulfuric acid such that the acidic aqueous halide solution generated is a hydrohalous

20 acid with a precipitate of the metal sulfate simultaneously forming and being removed with the second leached solids to be discarded as residue.

Usually the target metal recovery stage comprises a precipitation stage in which a precipitate of the target

25 metal is formed by adding a precipitation agent to the solution. This is a simple and expedient way of removing the or each target metal. When the oxidised metalliferous material comprises more than one target metal, a respective precipitation stage can thus be provided for

30 each target metal. These stages may be arranged in the process in series.

Depending on the type of oxidised metalliferous material, the leaching stage may comprise first and second

leaching stages that operate in a counter-current configuration, whereby:

- the oxidised metalliferous material is added to the first leaching stage to contact the solution and leach target metal into solution; and
- the solution from the first leaching stage is separated from first leached solids and passed to the target metal recovery stage; and
- the first leached solids are passed to the second leaching stage to be mixed with the acidic aqueous halide solution generated in the acid generation stage; and
- the solution from the second leaching stage is separated from second leached solids and passed to the first leaching stage, and the second leached solids are discarded as residue.

By employing a two-stage leaching process, target metal(s) can be partially leached from the oxidised metalliferous material in the first leaching stage, and can be further leached into solution in the second leaching stage by contacting the first solids with the hydrohalous acid. Then, leached target metal(s) from the second leaching stage can be returned with the solution to the first leaching stage, and thereafter can pass with the separated solution from the first leaching stage to the target metal recovery stage.

Further, when the solids from the first leaching stage are passed to the second leaching stage they are, in effect, contacted with a solution of relatively high acidity (ie. compared to the solution acidity in the first leaching stage) such that a proportion of remaining target metal in the solids is then leached into the solution for subsequent recovery.

In one form a portion of the solution from the second

leaching stage is not passed to the first leaching stage but is diverted to the acid generation stage, whereby after the sulfuric acid is added to this solution the acidic aqueous halide solution is generated for feeding to the second leaching stage to mix with the first leached solids. This stage allows for a metal sulfate precipitate to be formed and easily separated out from the acidic aqueous halide solution, which metal sulfate may be of a relative high purity. For example, the metal of the metal halide solution can be one that forms a precipitate with the sulfate anion of the sulfuric acid such that, the acidic aqueous halide solution generated in the acid generation stage is a hydrohalous acid, and such that a precipitate of the metal with sulfate anion forms.

In addition, prior to passing the acidic aqueous halide solution to the second leaching stage, any precipitate of the metal formed with the sulfate anion can be removed.

In addition, whilst an anion of the precipitation agent can cause target metal precipitation, the agent may also be used to introduce the metal of the metal halide solution (eg. the precipitation agent cation may be calcium). Thus, addition of the precipitation agent can maintain a desired concentration of that metal in solution, and to balance the process the metal may later be removed as a metal sulfate precipitate when the hydrohalous acid is formed.

In addition, when the metal of the metal halide solution forms a precipitate with the sulfate anion and is removed in the acid generation stage, a corresponding amount of that metal can be added in the target metal recovery stage to maintain the desired concentration.

The oxidised metalliferous material may comprise more

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than one target metal, and a respective precipitation stage is provided for each target metal.

For example, when the oxidised metalliferous material includes iron, a proportion of that iron can be leached
5 into solution in the leaching stage, and at least a

The sulfuric acid may be added to the leaching stage to achieve a pH in the range 0 to 1 and a solution Eh of 600mV (ref Ag/AgCl). The solution in the leaching stage can have a temperature ranging from 85 - 110°C.

5 When the halide in the metal halide solution is chloride, total chloride concentration may be in the range of 6 to 8 M, and when the metal in the metal halide solution is calcium, at least 30g/l of CaCl_2 can be maintained in the leaching stage.

10 In a second aspect there is provided a process for leaching a target metal from an oxidised metalliferous material, the process comprising first and second leaching stages in which an acidic aqueous halide solution generated from sulfuric acid and used for leaching the
15 target metal into solution passes counter-currently therethrough, wherein the acid generated from sulfuric acid is added to or formed in the second leaching stage, and the oxidised metalliferous material is fed to the first leaching stage and contacted with a recycle of
20 residual acid in solution from the second leaching stage to leach the material and produce first leached solids, and wherein the solution is separated from the first leached solids and may be passed to target metal recovery, whereas the first leached solids are passed to the second
25 leaching stage for contact with the acidic aqueous halide solution for further leaching of the solids whilst producing the residual acid recycle solution.

30 The acid generated from sulfuric acid can be generated in a separate stage from the second leaching stage prior to being added thereto, or may be generated in the second leaching stage.

The process of the second aspect finds particular application where the oxidised metalliferous material includes iron, particularly at high levels. Thus a

In the LEACH process, a lateritic ore 10 (which can also be a pre-prepared laterite concentrate) is crushed and ground at 12 and is then fed to an optional two stage counter-current leaching process having a first leach stage 14 and an acid generation stage 16, which may also function as a second leach stage, both of which operate at atmospheric pressure. The counter-current two stage leach benefits H_2SO_4 consumption as compared to a single stage leach but is more complex. In addition, either leach stage 10 has the option of being run at higher pressures (and thus higher temperatures) using an autoclave (eg. to minimise H_2SO_4 consumption and increase target metal extraction efficiencies, although increasing capital and operating costs).

15 Whilst a single stage leach can be used for simplicity and cost, the actual configuration used depends on the metalliferous material feed composition. With feed variation, the degree of benefit of H_2SO_4 consumption will vary and the two stage configuration may or may not be 20 required.

An acidic aqueous calcium chloride solution is passed through stage 16, the solution having a pH in the range of 0-1. This pH is achieved through the addition of sulfuric acid at levels sufficient to leach into solution target 25 metals such as nickel, cobalt and precious metals. The solution leaches the already partially leached laterite residual solids that are received from leach stage 14 via a thickening stage 18.

30 In stage 16 the solution has a temperature in the range of 85 to 110°C, an Eh controlled at ~600mV (versus Ag/AgCl), and a total chloride concentration in the range of 6 to 8M. However, the required solution for leaching depends on the mineralogy of the metalliferous material, in particular the types and quantities of acid

clear liquor overflow is passed to the PURIFICATION process and the solids underflow is passed to stage 16.

In the PURIFICATION process the clear liquor overflow is first passed to an iron removal stage 24, where calcium carbonate is added to cause haematite (Fe_2O_3) to form and precipitate (described below). The haematite is filtered out at separation stage 26.

Optionally, where copper has been used in the leaching process to enhance oxidation, the copper is next removed from the liquor at copper precipitation stage 28 by the addition of calcium carbonate, and is filtered out at separation stage 30. The copper residue can be reclaimed, or recycled back to the leaching process for re-use, as recycle 32.

The liquor is now passed to a precious metal recovery stage 34 where NaSH is added to precipitate out the precious metals (described below). The precious metals are filtered out at separation stage 36 and recovered by smelting etc.

Next, the liquor is passed to a nickel/cobalt recovery stage 38 where slaked lime ($\text{Ca}(\text{OH})_2$) is added to precipitate out the nickel and cobalt. The nickel and cobalt are filtered out at separation stage 40 and are then recovered. Any lead (Pb) in the ore can also be recovered at this stage.

Finally, where magnesium is present in the ore the liquor can be passed to a magnesium recovery stage 42, again where slaked lime ($\text{Ca}(\text{OH})_2$) is added to precipitate out the magnesium (described below). The magnesium is then filtered out at separation stage 44 and recovered, optionally with any other metals still present in the liquor.

The resulting purified liquor (CaCl_2 recycle solution 22)

is now returned to the LEACHING process.

Process of Figure 2

Figure 2 depicts a second alternative recovery process, where like reference numerals are used to denote similar or like process stages to those of Figure 1. The recovery process of Figure 2 is again depicted for a laterite feed but can be generalised to the recovery of one or more target metals from other oxidised metalliferous materials.

10 The recovery process of Figure 2 again comprises a two-stage leach process, with separated solution from the first leaching stage again being passed to target metal recovery stages (eg. precipitation and/or electrolytic recovery), but with solution recycle from the target metal
15 recovery stages direct to the first leaching stage.

In the two-stage leach process, a crushed and ground laterite feed 10 (having the metal concentration listed) is fed to the first leach stage 14 and then to second leach stage 16, both of which again operate at atmospheric
20 pressure. Again, either leach stage has the option of being run at higher pressures (and temperatures) using an autoclave.

As distinct from the process of Figure 1, the process of Figure 2 comprises a separate acid generation stage 17,
25 in which the acidic chloride solution is generated, and a second leaching stage. In this regard, like Figure 1, an H_2SO_4 solution is added to the acid generation stage 17. A diverted stream 19, being a portion of the leach recycle ("stream 9") is also added to the acid generation stage
30 17. The stream 9 comprises aqueous calcium chloride so that the diverted stream 19, which when contacted with the H_2SO_4 solution, generates the acidic chloride (HCl) solution and a calcium sulfate

precipitate (separated in stage 17 as a saleable by-product).

The acidic chloride (HCl) solution is passed to leach stage 16, the solution having a pH in the range of 0-1, sufficient to leach into solution target metals such as nickel, cobalt, iron, magnesium, precious metals etc. The acidic solution leaches the partially leached residual solids ("stream 8") that are received from leach stage 14 via solid/liquid separation stage 18.

In leach stage 16 the solution has a temperature in the range of 85 up to 110°C, with other parameters being similar to those described for the process of Figure 1.

The slurry of leached solids and solution is then passed from stage 16 to another solid/liquid separation stage 20, where residual solids are separated and discarded whereas part of the solution ("stream 5") is recycled to the first leach stage 14.

Again, this acid depleted recycle typically leaches a proportion of any iron in the feed into solution, with the solution parameters in stage 14 being similar to those described for the process of Figure 1.

The partially leached solids and solution are passed to solid/liquid separation stage 18 (as "stream 7") where a clear liquor overflow ("stream 6") is passed to the target metal recovery, the solids underflow ("stream 8") being passed to second leach stage 16.

In target metal recovery the clear liquor overflow is first passed to an iron precipitation stage 24, where calcium carbonate is added to cause haematite (Fe_2O_3) to form and precipitate. The haematite is separated out (eg. filtered) at separation stage 26.

A portion of the liquor ("stream 3") is recycled to the first leach stage 14, with the balance being passed to

a nickel/cobalt removal stage 38. In stage 38 slaked lime (Ca(OH)_2) is added to precipitate out the nickel and cobalt, which are then separated out (eg. filtered) at separation stage 40, for subsequent recovery.

5 A portion of the liquor ("stream 2") is again recycled to the first leach stage 14 whereas, to separate out magnesium present in the feed, the balance of liquor is passed to a magnesium removal stage 42. In stage 42 again slaked lime (Ca(OH)_2) is added to precipitate out the
10 magnesium. The magnesium is then separated out (eg. filtered) at separation stage 44, for subsequent recovery. The separated liquor from stage 44 ("stream 1") is recycled to the first leach stage 14, (combining with streams 2 and 3 as stream 4).

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Examples

Non-limiting examples of the processes described above will now be provided.

20 Example 1

A first process, hereafter referred to as the Intec Oxidised Metalliferous Materials Process (IOMMP) was developed as a halide-based alternative for the recovery of nickel and associated by-products from lateritic
25 deposits. Previously the development of such deposits was generally by way of pressure acid leach (PAL) or high pressure acid leaching (HPAL).

The IOMMP employed a chloride medium, as opposed to the conventional sulfate medium in PAL and HPAL. The main
30 advantage of the chloride medium is the ability to operate the leach at atmospheric pressure, without reliance on pyrohydrolysis to recover HCl for leaching and MgO for liquor purification.

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